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TEXAS UNIV AT AUSTIN DEPT OF CHEMISTRY
SYNTHESIS OF ORGANOFLUORINE COMPOUNDS BY DIRECT FLUORINATION. (U)
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8. PUBLICATIONS:

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A. D. BLOSE
Technical Information Officer

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In the early part of this Air Force sponsored program, we established that even hydrocarbons presenting the most difficult synthetic problems could be converted to fluorocarbons¹ in reasonable yield. (See fig. 1.) It became clear from these experiments that direct fluorination was capable of competing with techniques such as cobalt trifluoride reactions, electrochemical cell techniques, and conventional organic techniques on difficult synthetic projects often resulting in higher yields and novel compounds.

Undoubtedly, one of the most important contributions of the previous Air Force program was to establish viable synthetic techniques for the preservation of functional groups on organic compounds during fluorination.^{2,3,4} These techniques have led to a variety of new oxygen containing fluorocarbons. (See fig. 2) Striking contributions of the initial manuscript were the first fluorination process capable of preserving ester linkages, the first synthesis of perfluorodioxane and high yield synthesis for perfluoro acid fluorides. As is evident from this study, the previous synthesis for perfluoro "glyme" involved the electrochemical fluorination and cleavage of dioxane to give a 3% yield. The synthesis by direct fluorination of this technique produced perfluorodioxane in a 40% yield, and perfluoro "glyme" can now be prepared in 90% yield from the corresponding hydrocarbon ether.

Since 1975 the fluorination techniques have been refined such that one could say with confidence that almost any of the compounds

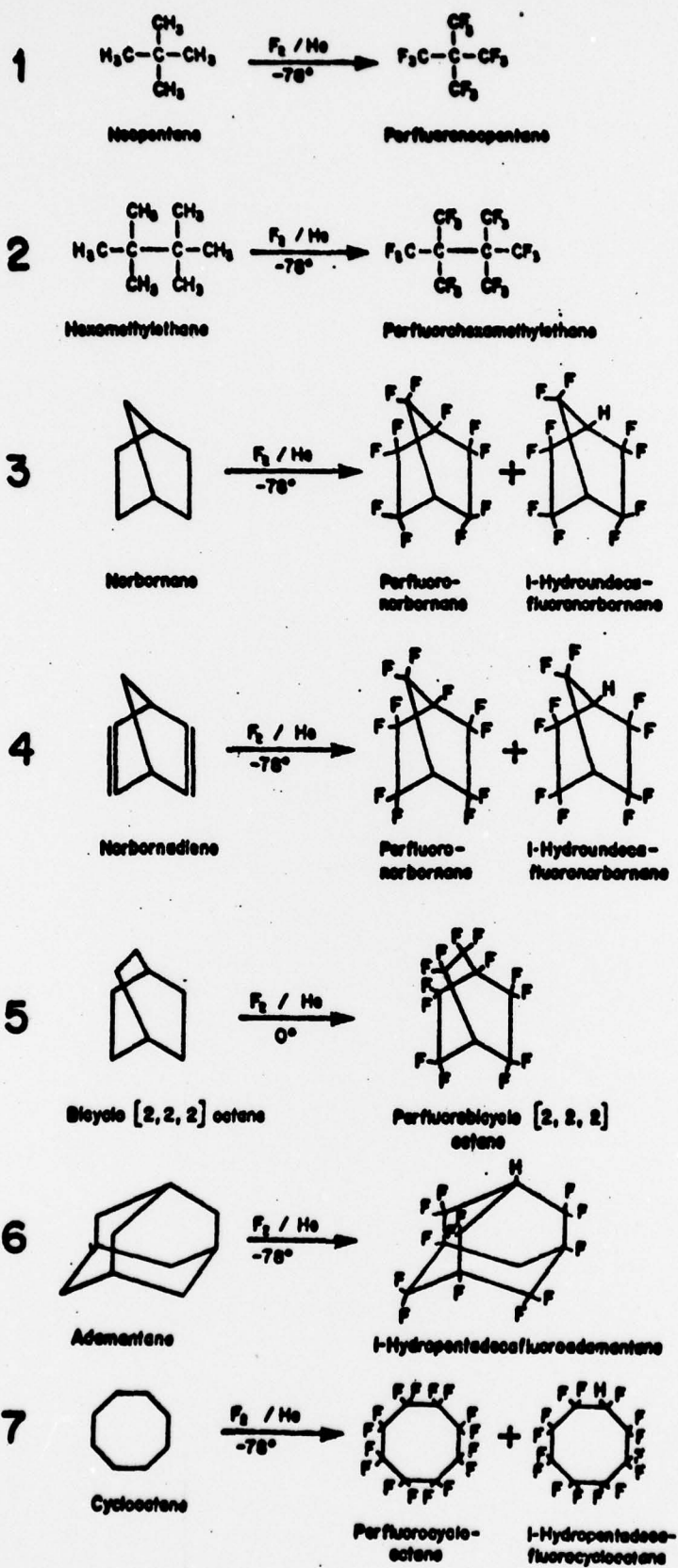
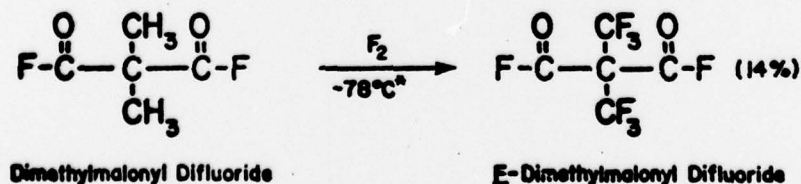
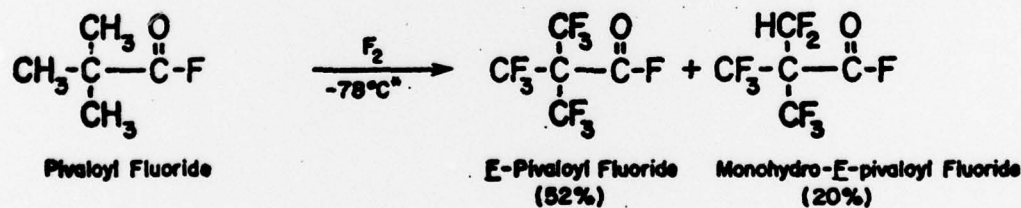
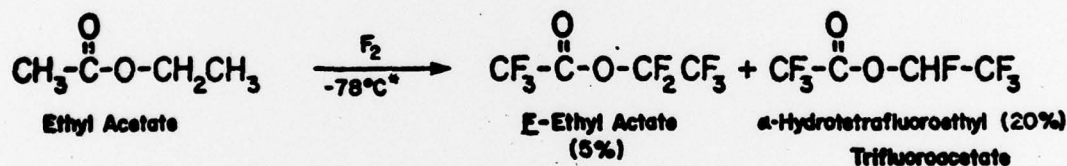
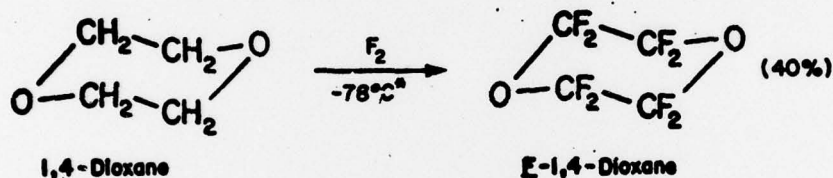
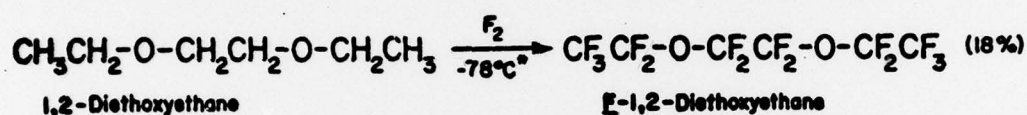
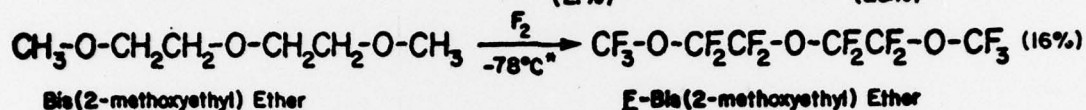
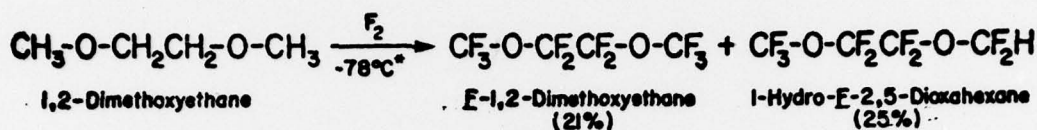


Fig. 1

Direct Fluorination of Oxygen Containing Hydrocarbons



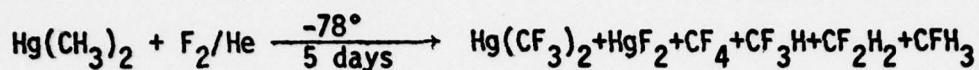
*Coldest Temperature of Gradient

Figure 2

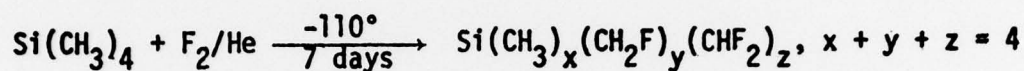
prepared in these earlier studies could now be obtained in yields at least double those of the original publications. For example, 90% yields of perfluoroneopentane have been obtained and yields of perfluoro-adamantanes in the 30-50% have been common when we have been called upon for samples of such compounds to meet needs in other laboratories and for derivative synthesis and physical studies in our research program.

The capability to prepare new fluorocarbon and functionalized fluorocarbon materials when they are needed is indeed an important one. It is still true in 1977 that there are many basic organic structures such as the previous example of dioxane, for which the fluorocarbon analogs are not known and unknown properties remain to be speculated upon. For example there are many known organic solvents for which there are not corresponding analogs. Should new compounds of this class be available in reasonable quantity, there would be much interest in their properties. Of course organofluorine compounds have a track record as one of the most valuable classes of compounds with respect to practical uses. This is especially true when properties associated with extreme stability, or on the other hand, properties associated with extreme reactivity are desirable. Both are available in fluorine chemistry.

There are a number of speculative efforts which have been recently successful in our laboratory which offer opportunities for new research efforts in the coming few years. One of the most surprising was the development of the ability to preserve metal-carbon bonds during direct fluorination. Initially, it was found⁵ that the low temperature fluorination of bistrimethylmercury gave low yields (7%) of bistrifluoromethylmercury:



This experiment added encouragement to our effort in this area. Subsequently the reaction of fluorine with tetramethylsilane produced a series of fluorinated silanes.⁵

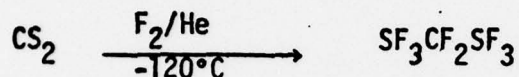


It was quite encouraging that the overall yield of polyfluoro-tetramethylsilanes was 70-80% indicating that at least that percentage of carbon-silicon bonds survive the fluorination process. An idea of the range of the products obtained from this reaction can be obtained from glancing at Table I - Table III on the next pages.

The most exciting experiment so far in fluorination of organo-metallic compounds is the synthesis of tetrakis(trifluoromethyl) germane in 63% yield on a two gram scale from tetramethylgermane.^{6a} Also under milder conditions it became clear that partially fluorinated tetramethylgermanes similar to the silane materials could be isolated under conditions different from those used to optimize the yield of $\text{Ge}(\text{CF}_3)_4$. The major products obtained under these conditions are listed in Tables IV through VI. A summary of work in this area is in press in Journal of Organometallic Chemistry.^{7b} Additionally, a description of the reactions of fluorine with tetramethyltin is to be published in Inorganic Chemistry. There are many new possibilities in this area. Certainly this represents an extreme in our endeavor to push the technique of controlling reactions of elemental fluorine toward its limits.

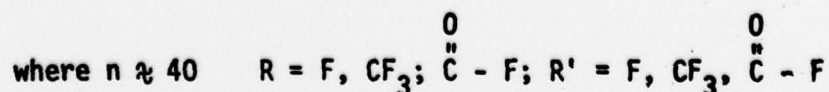
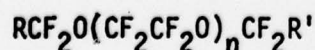
Another recent effort which forecasts any unexpected sensitivity

to be exploited in the next three year program is that of controlled oxidation of organic and inorganic compounds. As we have found much to our delight, the oxidation of sulfur can be controlled such that fluorination to a four coordinate is possible.⁷ Carbon disulfide was reacted with fluorine at low temperatures to produce difluoromethylene-bis(sulfur)trifluoride:



More extreme conditions may be employed to prepare the compound $(\text{SF}_5)_2\text{CF}_2$ if the six coordinate product is desired. A number of previous studies of the oxidation of carbon disulfide using other fluorination techniques have been reported, however, the isolation of practical quantities of $\text{SF}_3\text{CF}_2\text{SF}_3$ has not been previously reported. We have determined that this is not an isolated observation in main group chemistry from other studies which are in progress. This study provides an inkling of a number of developments based on this principle which will be pursued to establish wide application.

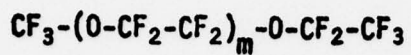
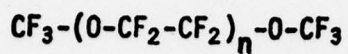
Recent work in our laboratory has also been focused toward the high temperature fluorination and cleavage of high molecular weight fluorinated polyethylene oxide to produce new discrete high boiling polyether materials.⁸ Controlled direct fluorination of polyethylene oxide results in the production of an oligomer which has a degree of polymerization of about 40 units and is composed of a mixture of nonfunctional, mono-functional, and difunctional polyethers of the perfluoroglyme structure:⁹



These materials have been partially separated, but their full characterization has taken a temporary back seat to the synthesis of slightly lower molecular weight perfluoro polyethers. By raising the fluorination temperature to 120° , to promote fragmentation, we have recently reported the synthesis of a series of⁸ perfluoro polyethers. The range of products which have been characterized is shown in Tables VII and VIII. At 120° if 40 grams of starting material are employed, the yields of volatile materials such as those shown in the tables are 9 grams plus over 40 grams of solid fluorocarbon. However, since this paper has been written, we have been extracting the involatile solids with organic solvents and obtaining substantial quantities of higher molecular weight perfluoro polyethers. These compounds range from very high boiling liquids to oils and wax-like materials. One of the initial aspects of the new program will be to fully characterize these materials and study their physical properties which appear to be most unusual.

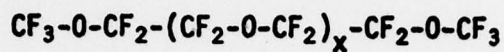
The fluorination at 120° or above serves to eliminate most of the acid fluoride functionalities which occur on the polyethylene structure. We have isolated some lower molecular weight functionalized polyethers in this process. However, under these conditions, the conversion leading to preservation of the acid fluoride group does not constitute a quantity such that there is a viable synthetic conversion. Other techniques which we are proposing will lead to the high molecular weight functional polyether materials.

We, of course, realize that there are other routes to perfluoro polyethers such as the polymerization of tetrafluoroethylene oxide, which has been under development by industrial firms like DuPont,

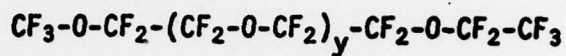
Table VII

Compound	m.p.	b.p.	Mole % of Volatile Prod. Mixture
n = 1			14.6
m = 1			7.6
n = 2		66 → 66.5	8.7
m = 2		81.5 → 82	4.9
n = 3	-82 → -80.5	104.5 → 105	8.1
m = 3	-80 → -78	117.5 → 118.5	5.7
n = 4	-71 → -69.5	138 → 138.5	6.8
m = 4	-60.5 → -60	146.5 → 148	5.3
n = 5	-47 → -46	164 → 164.5	5.9
m = 5	-47 → -46	173.5 → 174	4.3

Table VIII

 ^{19}F NMR Data

a b c



a b c c c c d

SHIFT in ppm vs. 1% aq. TFA (ext.)

(Relative Intensity)

Compound	a (trip.)	b (quart.)	c (sing.)	d (sing.)	Jab (in Hz)
x = 0	-16.3 (3)	18.3 (2)			10
y = 0	-16.3 (3)	18.2 (2)	16.2 (4)	15.0 (3)	10
x = 1	-16.4 (3)	18.2 (2)	16.1 (2)		9
y = 1	-16.6 (3)	18.0 (2)	16.0 (8)	14.8 (3)	9
x = 2	-16.6 (3)	18.1 (2)	16.0 (4)		9
y = 2	-16.7 (3)	18.0 (2)	15.9 (12)	14.7 (3)	9
x = 3	-16.6 (3)	18.0 (2)	15.9 (6)		9
y = 3	-16.8 (3)	17.8 (2)	15.8 (16)	14.6 (3)	10
x = 4	-16.8 (3)	17.8 (2)	15.8 (8)		10
y = 4	-16.7 (3)	17.9 (2)	15.8 (20)	14.6 (3)	10

Montecatini Edison and P.C.R. Our direct fluorination process, other than providing unique methods to specific compounds, offers the promise of relatively inexpensive syntheses. The hydrocarbon starting material, polyethylene oxide, costs less than 6¢ per pound and fluorine, although \$10 - \$12/lb. in laboratory quantities, is available at less than \$3.00 per pound if routed directly from an electrochemical cell. The bottling of elemental fluorine increases the cost substantially. Currently, prices as high as \$100/lb. are not uncommon for some commercially available perfluoroether material.

AFOSR Program Manager: Dr. A. Matuszko

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